

# PATENT SPECIFICATION (11) 1438719

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## (54) POLYMERIZATION OF CATIONIC MONOMERS

(71) We, CALGON CORPORATION, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Pittsburgh, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of cationic polymers useful as sludge dewatering agents and in certain other fields.

The present invention is based on the discovery that cationic polyelectrolytes highly effective as flocculants may be produced by the inverse emulsion polymerization of water-soluble cationic monomers in the presence of a crosslinking polyolefinic unsaturated comonomer.

In accordance with the present invention, cationic water-soluble copolymers are produced by (a) forming an aqueous solution of a cationic monomer and a water-soluble polyunsaturated monomer copolymerizable with it, (b) emulsifying the solution thereof in a water-insoluble organic liquid, and (c) polymerizing the monomers by free-radical generation.

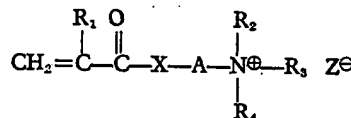
In solution or suspension polymerization of cationic monomers including the quantities of crosslinking polyolefinic unsaturated comonomers used in this invention, the resulting polymer is crosslinked and not effective as a flocculant or dewatering agent. The use of the inverse emulsion technique allows relatively high quantities of polyunsaturated comonomers to be utilized yet results in water-soluble or dispersible products.

The cationic monomers useful in the practice of this invention include dimethyl diallyl ammonium chloride (which is not a crosslinking agent), acryloxyethyl trimethyl ammonium chloride, methacryloxyethyl trimethyl ammonium chloride, vinyl benzyl trimethyl ammonium chloride, methyl (vinyl pyridinium) ammonium chloride, 3 - methacryloxy-(2 - hydroxy propyl) trimethyl ammonium

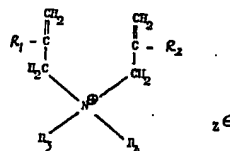
chloride, and 3 - acrylamido - 3 - methyl

butyl trimethyl ammonium chloride.

Cationic monomers of the formula



where R<sub>1</sub> is hydrogen or methyl; R<sub>2</sub> is hydrogen or C<sub>1-4</sub> alkyl; each of R<sub>3</sub> and R<sub>4</sub> is hydrogen, C<sub>1-12</sub> alkyl, benzyl or hydroxyethyl or R<sub>3</sub> and R<sub>4</sub>, together with the nitrogen atom to which they are both attached, form a cyclic ring containing one or more hetero atoms; Z is the conjugate base of an acid with a dissociation constant greater than 1 × 10<sup>-3</sup>; X is oxygen or imino; and A is an alkylene group; or a cationic monomer group derived from a compound having of the formula:



where each of R<sub>1</sub> and R<sub>2</sub> is hydrogen or methyl; R<sub>3</sub> is hydrogen, C<sub>1-12</sub> alkyl or benzyl; R<sub>4</sub> is hydrogen, C<sub>1-12</sub> alkyl, benzyl or hydroxyethyl; and Z is as defined above; may be used.

The crosslinking or branching comonomers employed in this system include tri and tetra allyl ammonium salts, methylene bisacrylamide, poly allyl ethers of polyhydroxyl compounds, e.g. poly allyl sucrose, diallyl sorbitol, and other water-soluble polyolefinic unsaturated compounds known to those skilled in the art of radical polymerization that normally (in systems other than inverse emulsion) lead to the formation of three-dimensional networks when used in high proportions. A

complete list of such compounds applicable to this invention would be prohibitively long. Any polyolefinic unsaturated compound that would lead to insoluble polymer when co-

polymerized with other monomers by solution, suspension or bulk methods could be used in our invention, as part of a water-soluble polymerization system.

The method for producing these compositions is similar to the inverse emulsion polymerization technique of U.S. Patent No. 3,284,393, applied to different polymerization systems. In this method certain water-soluble cationic monomers and crosslinking agents are dispersed with the addition of a surfactant in a water-insoluble liquid, e.g. a hydrocarbon. A radical generating catalyst is added and the temperature maintained at a suitable value until the polymerization is essentially complete. The polymerized emulsion is a white-to-semitransparent fluid. Depending upon the surfactant, the emulsion may be dissolved directly into water for use or the polymer isolated by evaporation of the solvent or solvent precipitation.

The specific embodiments of this invention are illustrated by the following examples, some of which are solution systems included for comparison.

#### EXAMPLE 1 Solution Polymerization of Dimethyl Diallyl Ammonium Chloride (DMAAC)

In a one-liter four-neck resin pot equipped with a mechanical stirrer, thermometer, condenser and purge tube was placed 492 grams of 55 percent aqueous DMAAC. The pH was adjusted to 6.0 with dilute hydrochloric acid and the mixture was heated to 50°C and urged with nitrogen for one hour with stirring. One milliliter of a 5 percent Na<sub>2</sub>EDTA solution was added followed by 7 milliliters of a 75 percent solution of *t*-butylperoxy-pivalate in mineral spirits. The purge tube was lifted above the surface of the liquid and a nitrogen blanket maintained throughout the rest of the reaction. The solution began to polymerize in 15 to 30 minutes and the reaction was mildly exothermic. The temperature was maintained through the use of external cooling. At the end of 3 hours, stirring was impossible because of the viscosity of the reaction mixture. After 18 hours at 50±2°C the conversion to polymer had levelled off at 95 percent. A 1 percent solution of this product in distilled water was completely free of insoluble gel.

#### EXAMPLE 2 Solution Polymerization of DMAAC, including 0.1 Mole Percent Triallyl Methyl Ammonium Chloride

The procedure was identical to that of Example 1, except that 0.1 mole percent of triallyl methyl ammonium chloride was added

to the reaction. A 1 percent solution of the resulting product partially dissolved with the remaining portion as highly hydrated gel. This crosslinked insoluble material is easily distinguished by those skilled in the art of polyelectrolytes.

#### EXAMPLE 3 Emulsion Polymerization of DMAAC

In a one-liter four-neck flask equipped with a stirrer, thermometer, condenser, purge tube, heating mantle and automatic heat-regulating device was placed 321.5 grams of benzene, 138.5 grams of 72.2 percent aqueous DMAAC and 40 grams of a 20 percent aqueous solution of sodium octyl phenoxyethoxy-2-ethanol sulphate. The mixture was stirred at 170 to 180 rpm with a paddle stirrer and heated to 50±1°C. The suspension was purged with nitrogen gas for 1 hour. 1.4 milliliters of a 0.351 gram per 100 milliliters solution of ferrous ammonium sulphate hexahydrate was added, followed by 0.336 milliliter of *t*-butylperoxypivalate (75 percent in mineral spirits). The solution was then stirred for 20 hours at 50°C under a nitrogen blanket.

The polymer was isolated by evaporating the benzene under ambient conditions. The final product was a glassy solid. A 1 percent solution of this polymer showed no evidence of insoluble gel.

#### EXAMPLE 4 Emulsion Polymerization of DMAAC, Plus 0.4 Mole Percent Triallyl Methyl Ammonium Chloride

The procedure of Example 3 was repeated except that 0.4 mole percent triallyl methyl ammonium chloride was added to the DMAAC solution prior to polymerization. A 1 percent solution of the resulting product showed no evidence of insoluble gel.

#### EXAMPLE 5 Solution Polymerization of 3 - Acrylamido-3 - Methyl Butyl Trimethyl Ammonium Chloride (AMBTAC)

The equipment of Example 1 was used. A solution of 150 grams of AMBTAC in 262.5 grams of distilled water, was adjusted to have a pH of 9.5 and was added to the reactor. The monomer solution was heated to 35°C and purged for 1 hour with nitrogen gas. 0.263 milliliters of a 75 percent solution of *t*-butylperoxypivalate in mineral spirits was added (1.5×10<sup>-3</sup> moles per mole of monomer). After approximately 25 minutes the polymerization began, as evidenced by an increase in viscosity and a slight increase in temperature. The solution was maintained at 35±5°C for 4 hours. A 1 percent solution of the resulting polymer was completely soluble.

## EXAMPLE 6

Solution Polymerization of AMBTAC with 0.1 Mole Percent Methylenebisacrylamide

- The procedure and equipment of Example 5 was used except that 0.1 mole percent methylenebisacrylamide (MDA) was added. A 1 percent solution of the final gel in water contained considerable amounts of highly hydrated gel typical of crosslinked polyelectrolytes. Higher levels of MBA produce progressively greater amounts of gel.

## EXAMPLE 7

Emulsion Polymerization of AMBTAC

- In an eight ounce pop bottle was placed 62 grams of benzene, 20 grams of AMBTAC dissolved in 10 grams of water, and 8 grams of a 20 percent aqueous solution of octyl phenoxethoxy (2) ethanol sodium sulphate. The bottle was sealed with an airtight septum. Two syringe needles were inserted into the bottle. The bottle was then placed in a constant temperature bath set at 50°C and agitated by shaking. Nitrogen gas was purged into the bottle through one syringe needle, the other needle serving as a vent. After 1 hour the needles were removed. 0.28 milliliter of a 0.351 gram per 100 milliliters solution of ferrous ammonium sulphate hexahydrate was injected into the bottle, followed by the injection of 0.07 milliliters of a 75 percent solution of *t*-butyl peroxyphosphate in mineral spirits. The bottle was agitated in the constant temperature bath for 20 hours. The product was isolated by adding the benzene emulsion to acetone, filtering the product and drying. A 1 percent solution of the final product was completely soluble in water.

## EXAMPLE 8

Emulsion Polymerization of AMBTAC with 0.4 Mole Percent Methylenebisacrylamide (MBA)

- The techniques of Example 7 was used except that 0.4 mole percent MBA was added before polymerization. The resulting polymer was completely soluble in water at 1 percent.

- The polymers of the invention are useful in flocculating solid particles in aqueous suspension, as in the clarification of water. For this purpose they may be added to the aqueous suspension in amounts as small as 0.1 ppm up to 20 ppm. A floc will form almost immediately and will settle in a short time, clarifying the water.

- The polymers of Examples 1 to 8 were tested for their ability to improve the rate of water release of activated sewage sludge. Activated sewage sludge is known to be extremely difficult to filter on vacuum filters commonly used in municipal waste treatment. The laboratory test used to simulate the equipment is the Buchner Funnel Test. A portion of sludge is treated with the poly-

electrolyte. The sample is poured into the Buchner funnel containing a standard filter paper and a standard vacuum is applied. The time to reach a specific volume of water drawn from the sludge is used as a measure of the effectiveness of the polymer. The shorter the time, the more effective the polymer in this application. In the test shown in Table I, 500 milliliters of sludge was treated at the dosage shown and the time was recorded when 400 milliliters of filtrate had been collected.

TABLE I  
Buchner Funnel Test Data  
Dosage=100 ppm

Samples	Time (Seconds)	
Example 1	277	80
Example 2	>600	
Example 3	486	
Example 4	94	
Example 5	>600	
Example 6	347	85
Example 7	>600	
Example 8	125	

The results of this test demonstrates that polymers of high performance are obtained by the emulsion process including a cross-linking agent.

The amount of branching (crosslinking) agent that can be used in solution, suspension or bulk polymerizations is extremely small. If one attempts to use the amount of branching agent contemplated in this invention only solvent-insoluble gels are formed. Such materials have no utility as water-soluble polymers. As shown in the examples, only ineffective products are obtained from solution polymerizations containing a branching agent. However, when the same or higher amounts of the branching agent are used in combination with emulsion polymerization techniques, a highly effective product is obtained. The examples also show that the emulsion polymerization techniques itself does not produce effective product without the addition of a branching agent. It is this synergistic combination of a branching agent and the emulsion polymerization technique that is unexpected and the essence of this invention.

The proportions of the components of the emulsion vary depending upon the components chosen. This invention is limited to water-soluble cationic monomers capable of producing water-soluble polymers by solution polymerization by radical mechanisms. The suspending medium can be any water-insoluble organic fluid that does not interfere with radical polymerization. The preferred suspending media are benzene, perchloroethylene, high aromatic distillates and saturated hydrocarbons such as hexane and mineral

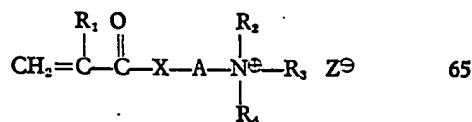
oil. The surface active agent and the amount used depend upon the nature of the cationic monomer and the suspending medium chosen. For dimethyl diallyl ammonium chloride and benzene, the preferred surface-active agent is sodium octyl phenoxy - 2 - ethanol sulfate. However, if mineral oil were used in the place of benzene, the preferred surfactant would be oleyl poly ethoxy (2) ethanol ether.

Each combination of cationic monomer and suspending medium will perform best with a specific surface-active agent or combination of surface-active agents as may be determined by persons skilled in the art. The proportions of these components should be balanced to obtain a stable emulsion polymerization.

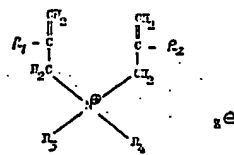
The cationic monomer may be present in the aqueous phase in amounts from 5 to 95 percent by weight of the aqueous phase, and the crosslinking agent about 0.005 to 5.0 mole percent based on the cationic monomer. The surfactant or emulsifier may be 0.5 percent to 10 percent by weight of the total mixture. The water-insoluble liquid forming the continuous phase of the inverse emulsion preferably makes up from 25 percent to 90 percent by weight of the total emulsion. The free radical polymerization initiator is preferably present in amounts from  $10^{-7}$  to  $10^{-1}$  mole per mole of cationic monomer.

#### WHAT WE CLAIM IS:—

1. A method of forming cationic water-soluble co-polymers that comprises (a) forming an aqueous solution of a cationic monomer and a water-soluble poly-unsaturated monomer copolymerizable with it, (b) emulsifying the solution thereof in a water-insoluble organic liquid, and (c) polymerizing the monomers by free-radical generation.
2. A method as claimed in Claim 1 in which the concentration of cationic monomer in the aqueous phase is from 5 to 95 percent by weight of the aqueous phase.
3. A method as claimed in Claim 1 or 2 in which the concentration of copolymerizable polyunsaturated monomer is from 0.005 to 5.0 mole percent based on the cationic monomer.
4. A method as claimed in any preceding claim in which the emulsification is promoted by adding a surface-active agent in an amount from 0.5 to 10 percent by weight of the total mixture.
5. A method as claimed in any preceding claim in which the amount of water-insoluble liquid is from 25 to 90 percent by weight of the total emulsion.
6. A method as claimed in any preceding claim in which from  $10^{-7}$  to  $10^{-1}$  mole of a free radical initiator is added per mole of cationic monomer.
7. A method as claimed in any preceding claim in which the cationic monomer has the general formula



where R<sub>1</sub> is hydrogen or methyl; R<sub>2</sub> is hydrogen or C<sub>1-12</sub> alkyl; each of R<sub>3</sub> and R<sub>4</sub> is hydrogen, C<sub>1-12</sub> alkyl, benzyl or hydroxyethyl or R<sub>3</sub> and R<sub>4</sub>, together with the nitrogen atom to which they are both attached, form a cyclic ring containing one or more hetero atoms; Z is the conjugate base of an acid with a dissociation constant greater than  $1 \times 10^{-3}$ ; X is oxygen or imino; and A is an alkylene group; or the cationic monomer has the formula:



where each of R<sub>1</sub> and R<sub>2</sub> is hydrogen or methyl; R<sub>3</sub> is hydrogen, C<sub>1-12</sub> alkyl or benzyl; R<sub>4</sub> is hydrogen, C<sub>1-12</sub> alkyl, benzyl or hydroxyethyl; and Z is as defined above.

8. A method of making a cationic polymer comprising forming an aqueous solution of from 5 percent to 95 percent by weight of dimethyl diallyl ammonium chloride and from 0.005 mole to 5 mole percent, based on the moles of dimethyl diallyl ammonium chloride, of methylene bisacrylamide, emulsifying the said solution in a water-insoluble liquid to form an emulsion of which the water-insoluble liquid forms from 25 to 90 percent by weight and polymerizing the monomer mixture.

9. A method of making a cationic polymer comprising forming an aqueous solution of from 5 percent to 95 percent by weight of dimethyl diallyl ammonium chloride and from 0.005 mole to 5 mole percent, based on the moles of dimethyl diallyl ammonium chloride, of methyl triallyl ammonium chloride, emulsifying the said solution in a water-insoluble liquid to form an emulsion of which the water-insoluble liquid forms from 25 to 90 percent by weight, and polymerizing the monomer mixture.

10. A method of making a cationic polymer comprising forming an aqueous solution of from 5 percent to 95 percent by weight of dimethyl diallyl ammonium chloride and from 0.005 mole to 5 mole percent, based on the moles of dimethyl diallyl ammonium chloride, of tetraallyl ammonium chloride, emulsifying the said solution in a water-insoluble liquid to form an emulsion of which the water-insoluble liquid forms from 25 to 90 percent

by weight, and polymerizing the monomer mixture.

- 5 11. A method as claimed in Claim 8, 9 or 10 in which the aqueous solution and the water-insoluble liquid are emulsified, with the water-insoluble liquid forming the continuous phase, in the presence of from 0.5 percent to 10 percent by weight, based on the total mixture, of a surface-active agent.

- 10 12. A method as claimed in any one of Claims 8—11 in which polymerization is initiated in the presence of from  $10^{-7}$  to  $10^{-1}$  mole of free-radical initiator per mole of cationic monomer.

- 15 13. A method as claimed in Claim 1 substantially as hereinbefore described in Example 4 or Example 8.

- 20 14. A water-soluble polymer made by a method as claimed in any one of Claims 1—7.

15. A water-soluble polymer made by a method as claimed in Claim 8.

16. A water-soluble polymer made by a method as claimed in Claim 9.

- 25 17. A water-soluble polymer made by a method as claimed in Claim 13.

18. A method of releasing water from activated sewage sludge comprising adding to it

an effective amount of a polymer as claimed in any one of Claims 14—17 and filtering the sludge. 30

19. A method of flocculating solid particulate matter in aqueous suspension comprising adding to the aqueous suspension from 0.1 ppm to 20 ppm by weight of a polymer as claimed in any one of Claims 14—17. 35

20. A method of making a cationic polymer comprising forming an aqueous solution of 5 percent to 90 percent by weight 3 - acrylamido - 3 - methyl butyl trimethyl ammonium chloride and 0.005 mole to 5 mole percent, based on the moles of 3 - acrylamido - 3 - methyl butyl trimethyl ammonium chloride, of a copolymerizable polyunsaturated crosslinking monomer, emulsifying the solution in a water-insoluble liquid to form an emulsion of which the water-insoluble liquid forms from 25 to 90 percent by weight, and polymerizing the monomer mixture. 40 45

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